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The Solvent Path in Square-Planar Substitutions. Kinetics and Mechanism for Reactions of Tetrachloroplatinate(II) and Aquachloroplatinates(II) with Halides, Thiocyanate and Dimethyl Sulfoxide

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The kinetics for the reactions between the six complexes $PtCl_n(H_2O)_{4-n}^{2-n}$; n = 0,1,2,3,4 (including cis- *and* trans-*isomers for n = 2) and the entering ligands Y = Cl^-, Br^-, I^-, SCN^-, and DMSO have been studied. The experiments with $PtCl_4^{2-}$ and* trans-*$PtCl_2(H_2O)_2$ give the usual two-term rate constant $k_{exp} = k_1 + k_2[Y]$, when no extra chloride has been added to the solutions. The parameter k_1 can be identified as the acid hydrolysis rate constant for $PtCl_4^{2-}$ and* trans-*$PtCl_2(H_2O)_2$, respectively. It is shown that both $PtCl_3H_2O^-$ and $PtCl(H_2O)_3^+$ are sufficiently reactive for all Y to be the intermediates in the k_1-paths of these two reactions. An associative process with the solvent is therefore probable.*

The entering ligand order for H_2O as leaving ligand is DMSO < Cl^- < Br^- < SCN^- < I^- (approximately 0.3:1:4:40:100) for the substrate complexes studied. DMSO is a bad entering ligand in spite of its large trans-*effect. The relative* trans-*effect Cl^-/H_2O and the relative efficacy of H_2O and Cl^- as leaving ligands depend on the nature of the entering ligand Y, whereas the relative* cis-*effect Cl^-/H_2O is independent of Y. This is compatible with an associative mechanism* via *a trigonal bipyramidal intermediate.*

Introduction

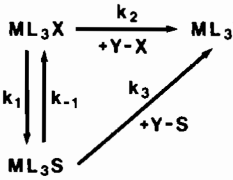
Ligand substitution reactions of square planar complexes of the type (1)

$$ML_3X + Y \rightleftarrows ML_3Y + X \qquad (1)$$

usually follow the two-term rate law (2) [1, 2].

$$\textit{Rate} = (k_1 + k_2[Y])\,[\text{complex}] \qquad (2)$$

The k_2-term is generally considered to correspond to an associative reaction between the complex and the entering ligand Y. There are some indications that the k_1-term might have its origin in a dissociative process *via* an intermediate with decreased coordination number [3], but the majority of experimental evidence for the k_1-term are compatible with an associative rate-determining reaction between the solvent and the complex, followed by a rapid substitution of the solvent molecule in the intermediate solvato complex by Y. The two paths can be described by the scheme (3).



(3)

If the intermediate ML_3S is present in steady-state concentrations, the pseudo first-order rate constant for excess entering ligand is described by (4).

$$k_{exp} = \frac{k_1}{1 + k_{-1}[X]/k_3[Y]} + k_2[Y] \qquad (4)$$

For $k_{-1}[X] \ll k_3[Y]$ eqn. (4) transforms to the usual expression (5).

$$k_{exp} = k_1 + k_2[Y] \qquad (5)$$

Necessary conditions for the associative mechanism (3) *via* ML_3S and eqns. (4) and (5) are that $k_3 \gg k_2$ ($\approx k_1/[Y]$) and that k_1 in eqns. (4) and (5) is identical to the rate constant for the solvolysis of the substrate complex ML_3X.

We here report kinetic studies on reaction (6)

$$PtCl_4^{2-} + Y \rightarrow PtCl_3Y^- + Cl^- \qquad (6)$$

for the entering ligands Y = Br^-, I^-, SCN^-, and DMSO. According to the model (3), $PtCl_3H_2O^-$ is the intermediate in the k_1-path. The rate constant k_1 for its formation by acid hydrolysis of $PtCl_4^{2-}$ has been determined previously [4]. We have checked the other necessary condition for the associative model (3), *viz.* $k_3 \gg k_2$ ($\approx k_1/[Y]$) by a separate investigation of reaction (7)

$$PtCl_3H_2O^- + Y \xrightarrow{k_3} PtCl_3Y^- + H_2O \qquad (7)$$

for Y = Cl^-, Br^-, I^-, SCN^-, and DMSO. We have also studied the reactions of other chloro aqua complexes with the entering ligands Y:

$$trans\text{-}PtCl_2(H_2O)_2 + Y \rightarrow trans\text{-}PtClY(H_2O)_2^+ + Cl^- \qquad (8)$$

$$cis\text{-}PtCl_2(H_2O)_2 + Y \rightarrow PtCl_2Y(H_2O) + H_2O \qquad (9)$$

$$PtCl(H_2O)_3^+ + Y \rightarrow trans\text{-}PtClY(H_2O)_2^+ + H_2O \qquad (10)$$

$$Pt(H_2O)_4^{2+} + Y \rightarrow PtY(H_2O)_3^{2+} + H_2O \qquad (11)$$

and report results for Y = Br^-, I^-, SCN^-, and DMSO for reactions (8) and (10), for Y = Cl^-, Br^-, I^-, SCN^-, and DMSO for reaction (9), and for Y = DMSO for reaction (11). $PtCl(H_2O)_3^+$ is the intermediate in the k_1-path for reaction (8). The results for reactions (8) and (10) therefore give a further possibility to check the conditions for the associative model (3). The present results together with published constants [6] for $Pt(H_2O)_4^{2+}$ also enable a quantitative evaluation of the rate parameters for reactions (6)–(11).

Mureinik [5] has reported that aqua complexes of platinum(II) do not react with thiocyanate. This is not compatible with our present findings and with other experimental evidence for reactions of aqua complexes, for instance refs. 4, 6, 10, 12–16, (*vide infra*).

TABLE I. Reaction Between $PtCl_4^{2-}$ and Entering Ligands Y. Wavelengths: 250 nm (Br^-), 310 and 330 nm (I^-), 310 nm (SCN^-), and 285 nm (DMSO).

Y	10^3 C_Y/M	10^3 $[Cl^-]_{added}/M$	$10^4 C_{Pt}/M$	pH	10^3 k_{exp}/s^{-1}
Br^-	10	–	0.2	1.000	0.040 ± 0.001
	100	–	0.2	1.000	0.046 ± 0.002
	500	–	0.2	1.000	0.063 ± 0.002
	1000	–	0.2	1.000	0.087 ± 0.003
I^-	1.0	200	0.4	7	0.031 ± 0.002
	2.0	400	0.4	7	0.049 ± 0.005
	3.0	600	0.4	7	0.070 ± 0.006
	4.0	800	0.4	7	0.090 ± 0.008
	5.0	995	0.4	7	0.110 ± 0.008
	10.0	990	0.05	7	0.21 ± 0.01
	10.0	990	0.05	4.0	0.25 ± 0.03
	25	975	0.05	7	0.53 ± 0.03
	50	950	0.05	7	1.06 ± 0.05
	50	950	0.05	4.0	1.05 ± 0.05
	100	900	0.05	7	2.1 ± 0.1
SCN^-	5	–	2.0	1.301	0.085 ± 0.005
	10	–	2.0	1.301	0.135 ± 0.008
	15	–	2.0	1.301	0.181 ± 0.010
	20	–	2.0	1.301	0.226 ± 0.010
	25	–	2.0	1.301	0.278 ± 0.010
	100	–	2.0	1.301	1.07 ± 0.10
	200	–	2.0	1.301	2.10 ± 0.15
	300	–	2.0	7	2.75 ± 0.25
	300	–	2.0	1.301	3.01 ± 0.20
	400	–	2.0	1.301	4.15 ± 0.20
	500	–	2.0	7	5.10 ± 0.30
	500	–	2.0	1.301	5.16 ± 0.25
DMSO	20	200	2.1	1.301	0.077 ± 0.003
	40	400	2.1	1.301	0.148 ± 0.005
	60	600	2.1	1.301	0.209 ± 0.006
	80	800	2.1	1.301	0.267 ± 0.010
	100	1000	1.1	1.301	0.329 ± 0.010
	200	1000	1.1	1.301	0.640 ± 0.015
	300	1000	1.1	1.301	0.930 ± 0.020
	400	1000	1.1	1.301	1.22 ± 0.030
	500	1000	1.1	1.301	1.53 ± 0.050

Experimental

Chemicals and Solutions

Potassium tetrachloroplatinate(II) (Johnson and Matthey) was used directly. Solutions of tetraaquaplatinum(II) perchlorate in 1.00 *M* perchloric acid were prepared as described previously [7]. Solutions of the other platinum(II) chloro aqua complexes were prepared immediately before use in the kinetics.

Solutions of trichloroaquaplatinate(II), $PtCl_3H_2O^-$, were obtained by slow addition at 40 to 50 °C of 20 ml 10 m*M* $AgNO_3$ (Merck's *p.a.*) to 10 ml 20 m*M* K_2PtCl_4 (which had first been aged for 15 min at 50 °C) and subsequent separation of the silver chloride precipitate.

Solutions of *cis*-dichlorodiaquaplatinate(II), *cis*-$PtCl_2(H_2O)_2$, were prepared by aging an aqueous solution of K_2PtCl_4 (0.2 or 0.4 m*M*) with sodium hydroxide (5 m*M*) for about 20 h at 25 °C and subsequent addition of an equal volume of 6.00 m*M* $HClO_4$ + 1.99 *M* $NaClO_4$, or 0.100 *M* $HClO_4$ + 1.90 *M* $NaClO_4$, or 1.00 *M* $HClO_4$ + 1.00 *M* $NaClO_4$.

Solutions of *trans*-$PtCl_2(H_2O)_2$ were prepared by aging $Pt(H_2O)_4^{2+}$ solutions (7.0 m*M* in 1.00 *M* $HClO_4$) with sodium chloride (50 or 75 m*M* in 0.950 or 0.925 *M* $NaClO_4$) for about 75 min at 25 °C. Solutions of *trans*-$PtCl_2(H_2O)_2$ having pH ~4 were obtained by subsequent addition of 1.00 *M* NaOH.

Solutions of chlorotriaquaplatinum(II), $PtCl(H_2O)_3^+$, were prepared by slow addition at room temperature of 20 ml 43 m*M* silver nitrate to 20 ml of a stirred solution of *trans*-$PtCl_2(H_2O)_2$ (7 m*M* with 36.0 m*M* chloride). After aging for about 24 h, the silver chloride precipitate (corresponding to one equivalent of chloride per platinum) was separated.

Ligand solutions were prepared from 1.00 *M* stock solutions of perchloric acid (Baker's *p.a.*), sodium perchlorate (Baker's *p.a.*, recrystallized), hydrochloric acid (Merck's *p.a.*), freshly distilled hydrobromic acid (Merck's *p.a.*), sodium iodide (Merck's *p.a.*), sodium thiocyanate (Mallinckrodt's *p.a.*), and from DMSO (BDH, freshly distilled in vacuum over calcium hydride). A 1.00 *M* sodium perchlorate–perchloric acid medium was used except for some experiments with DMSO and iodide, where the medium had to be 1.00 *M* sodium chloride–sodium perchlorate. For the experiments with thiocyanate at pH 4.6, the solutions contained a 0.2 *M* acetic acid (Merck's *p.a.*)/sodium acetate (A. Johnson, *p.a.*) buffer. For the used pH, formation of HSCN (pK_a = –1.8) [8] and $DMSOH^+$ (pK_a = –2.0) [9] were negligible. Protolysis of the aqua ligands of the platinum complexes (pK_a between about 4 and 7) [7, 10] did not influence the results.

Procedure

Large excess of entering ligand or complex gave pseudo first-order kinetics and suppressed the reverse reactions. Subsequent reactions were eliminated by

TABLE II. Reaction Between $PtCl_3H_2O^-$ and Entering Ligands Y. Wavelengths 230 nm (Cl^-), 250 nm (Br^-), 310 and 330 nm (I^-), 310 nm (SCN^-) and 285 nm (DMSO).

Y	$10^3\ C_Y/M$	$10^4\ C_{Pt}/M$	pH	$10^3\ k_{exp}/s^{-1}$
Cl^-	100	0.5	0.000	0.54 ± 0.03
	200	0.5	0.000	1.01 ± 0.06
	300	0.5	0.000	1.59 ± 0.68
	400	0.5	0.000	2.12 ± 0.11
	500	0.5	0.000	2.62 ± 0.13
Br^-	100	0.5	0.000	2.10 ± 0.20
	200	0.5	0.000	4.3 ± 0.4
	300	0.5	0.000	6.0 ± 0.6
	400	0.5	0.000	8.3 ± 0.8
	500	0.5	0.000	10.3 ± 1.0
I^-	5	0.2	7	1.85 ± 0.15
	5	0.8	7	2.1 ± 0.1
	10	0.2	7	3.85 ± 0.15
	10	0.8	7	3.7 ± 0.2
	25	0.2	7	9.55 ± 0.15
	25	0.8	7	9.0 ± 0.3
	25	0.4	4.0	9.5 ± 0.2
	50	0.2	7	19.2 ± 0.5
	50	0.8	7	18.9 ± 0.5
	50	0.4	4.0	19.4 ± 0.5
	75	0.2	7	29.7 ± 1.3
	100	0.2	7	39.6 ± 2.0
SCN^-	100	2.0	7	1.00 ± 0.10
	100	2.0	4.6	0.84 ± 0.04
	100	2.0	1.301	0.98 ± 0.08
	125	2.0	0.058	1.19 ± 0.10
	200	2.0	7	2.05 ± 0.20
	200	2.0	4.6	1.68 ± 0.08
	200	2.0	1.301	1.97 ± 0.17
	200	2.0	0.523	1.82 ± 0.13
	250	2.0	0.125	2.31 ± 0.15
	300	2.0	7	3.06 ± 0.30
	300	2.0	4.6	2.58 ± 0.13
	300	2.0	1.301	2.94 ± 0.10
	400	2.0	7	4.0 ± 0.3
	400	2.0	4.6	3.48 ± 0.17
	400	2.0	1.301	4.09 ± 0.20
	500	2.0	7	5.01 ± 0.30
	500	2.0	1.301	5.02 ± 0.10
	500	2.0	0.301	5.01 ± 0.10
DMSO	10	1.7	1.301	0.30 ± 0.05
	20	1.7	1.301	0.63 ± 0.10
	25	1.7	1.301	0.87 ± 0.10
	40	1.7	1.301	1.02 ± 0.12
	50	1.7	1.301	1.55 ± 0.16
	60	1.7	1.301	1.60 ± 0.16
	75	1.7	1.301	2.15 ± 0.20
	90	1.7	1.301	2.58 ± 0.20
	100	1.7	4.0	2.9 ± 0.3
	100	1.7	1.301	2.85 ± 0.25
	200	1.7	1.301	5.3 ± 0.3
	250	1.7	4.0	6.5 ± 0.4
	300	1.7	1.301	8.8 ± 0.5
	400	1.7	1.301	11.3 ± 0.5
	500	1.7	1.301	13.7 ± 0.7

extrapolation, and the wavelengths were chosen to minimize their influence as much as possible. The rate constants were calculated directly from the transmittance *vs.* time plots or from ordinary logarithmic plots using least-squares programmes. The temperature was (25.00 ± 0.02) °C.

Tables I to VI summarize the experiments on reactions (6) to (11) using excess ligand. A Zeiss PMQ II spectrophotometer with a recorder was used. Extra chloride was added to the $PtCl_4^{2-}$ solutions in the experiments with DMSO and iodide (*cf.* Table I). For Y = DMSO, addition of excess chloride ($[Cl^-]/[DMSO] \geqslant 2$) was necessary to suppress the subsequent reaction between DMSO and $PtDMSOCl_3^-$, which is not kinetically separable from reaction (6) [11]. For Y = I^-, addition of chloride ($[Cl^-]/[I^-] \geqslant 200$) for $[I^-] \leqslant 5$ m*M* suppressed formation of complexes having a mean ligand number $\bar{n}_I > 2$, which minimizes the influence of disturbing side reactions. It was also necessary to use low concentrations of platinum in these experiments, in order to prevent formation of dimeric iodo complexes.

TABLE III. Reaction Between *cis*-$PtCl_2(H_2O)_2$ and Entering Ligands Y. Wavelengths: 210 nm (Cl^-), 261 nm (Br^-), 330 nm (I^-), 310 nm (SCN^-), 285 nm (DMSO).

Y	$10^3\ C_y/M$	$10^4\ C_{Pt}/M$	pH	$10^3\ k_{exp}/s^{-1}$
Cl^-	10	0.2	1.600	1.0 ± 0.08
	30	0.2	1.600	2.8 ± 0.2
	50	0.2	1.600	4.5 ± 0.3
	100	0.2	1.600	8.9 ± 0.5
	300	0.2	1.600	26.6 ± 0.5
	500	0.2	1.600	40.9 ± 0.6
Br^-	5.0	1.51	0.000	2.0 ± 0.1
	10	1.51	0.000	3.5 ± 0.1
	20	1.51	0.000	7.3 ± 0.2
	25	1.51	0.000	8.3 ± 1.0
	30	1.51	0.000	13.3 ± 1.5
	40	1.51	0.000	15.3 ± 1.0
	50	1.51	0.000	16.5 ± 1.0
	100	1.51	0.000	30.5 ± 1.1
I^-	0.5	0.95	2.000	3.0 ± 0.5
	1.0	0.95	2.000	7.9 ± 0.6
	2.0	0.67	3.50	12.0 ± 1.0
	2.0	0.95	2.000	14.3 ± 0.9
	2.5	0.95	2.000	17.5 ± 1.0
	3.0	0.67	3.30	19.0 ± 1.0
	3.0	0.95	2.000	20.7 ± 2.0
	4.0	0.95	2.000	28.9 ± 1.2
	5.0	0.67	3.50	26.0 ± 2.0
	5.0	0.95	2.000	36.0 ± 2.0
SCN^-	2.0	1.0	1.600	8.0 ± 0.5
	5.0	1.0	1.600	16.0 ± 1.0
	10	1.0	1.600	32.0 ± 1.0
	15	1.0	1.600	48.0 ± 2.0
	20	1.0	1.600	63 ± 5
DMSO	50	1.5	1.301	1.23 ± 0.03
	100	1.5	1.301	2.46 ± 0.06
	200	1.5	1.301	5.20 ± 0.10
	300	1.5	1.301	7.4 ± 0.4
	400	1.5	1.301	10.1 ± 0.6
	500	1.5	1.301	12.7 ± 0.8

Reaction (11) for excess platinum was started by mixing 10 ml DMSO solution with 90 ml $Pt(H_2O)_4^{2+}$ solution. The concentrations after mixing are given in Table VI. The stability constant for $PtDMSO(H_2O)_3^{2+}$ is greater than $10^7\ M^{-1}$ [13], so the reverse reaction can be neglected. Samples were taken at intervals of time and mixed in a Durrum-Gibson stopped-flow spectrophotometer [12] with equal volumes of 10.0 m*M* HCl + 0.99 *M* $HClO_4$. Reaction (12) was recorded

$$PtDMSO(H_2O)_3^{2+} + Cl^- \rightarrow \textit{trans}\text{-}PtDMSOCl(H_2O)_2^+ + H_2O \qquad (12)$$

TABLE IV. Reaction Between *trans*-$PtCl_2(H_2O)_2$ and Entering Ligands Y. Wavelengths: 250 nm (Br^-), 320 nm (I^-), 290 nm (SCN^-), and 285 nm (DMSO).

Y	$10^3\ C_y/M$	$10^4\ C_{Pt}/M$	pH	$10^3\ k_{exp}/s^{-1}$
Br^-	50	2.0	0.000	0.40 ± 0.02
	100	2.0	0.000	0.80 ± 0.03
	250	2.0	0.000	1.80 ± 0.10
	350	2.0	0.000	2.40 ± 0.10
	450	2.0	0.000	3.30 ± 0.10
I^-	0.5	0.4	4.0	0.27 ± 0.03
	1.0	0.4	4.0	0.46 ± 0.05
	2.0	2.0	4.0	0.75 ± 0.05
	3.0	2.0	4.0	1.08 ± 0.10
	4.0	2.0	4.0	1.4 ± 0.1
	5.0	2.0	4.0	1.7 ± 0.2
	10	2.0	4.0	3.5 ± 0.5
	25	2.0	4.0	8.1 ± 0.7
	50	2.0	4.0	15.7 ± 1.0
	100	2.0	4.0	31.0 ± 1.0
SCN^-	0.5	1.0	1.600	0.26 ± 0.02
	1.0	1.0	1.600	0.40 ± 0.03
	3.0	1.0	1.600	1.05 ± 0.05
	5.0	1.0	1.600	1.67 ± 0.07
	25	1.0	1.600	7.8 ± 1.4
	50	1.0	1.600	14.6 ± 0.8
	100	1.0	1.600	28.0 ± 2.2
	200	1.0	1.600	58.0 ± 1.4
	275	1.0	1.600	79 ± 3
DMSO	100	2.0	1.600	0.23 ± 0.02
	200	2.0	1.600	0.42 ± 0.04
	300	2.0	1.600	0.53 ± 0.05
	400	2.0	1.600	0.67 ± 0.05
	500	2.0	1.600	0.81 ± 0.06

TABLE V. Reaction Between $PtCl(H_2O)_3^+$ and Entering Ligands Y. Wavelengths: 245 nm (Br^-), 295 nm (I^-), 280 nm (SCN^-), and 280 nm (DMSO).

Y	10^3 C_Y/M	10^4 C_{Pt}/M	pH	10^2 k_{exp}/s^{-1}
Br^-	5.0	2.0	1.600	0.8 ± 0.07
	10	2.0	1.600	2.0 ± 0.2
	15	2.0	1.600	2.7 ± 0.2
	20	2.0	1.600	3.6 ± 0.3
	25	2.0	1.600	3.2 ± 0.2
	30	2.0	1.600	4.5 ± 0.2
	40	2.0	1.600	6.6 ± 0.4
	50	2.0	1.600	8.8 ± 0.5
I^-	0.25	0.3	1.600	1.00 ± 0.05
	0.50	0.3	1.600	2.14 ± 0.15
	1.0	0.3	1.600	3.85 ± 0.20
	1.4	0.3	1.600	5.35 ± 0.10
	2.0	0.3	1.600	7.79 ± 0.10
SCN^-	1.0	1.0	1.600	1.55 ± 0.10
	2.0	1.0	1.600	3.25 ± 0.30
	3.0	1.0	1.600	4.70 ± 0.30
	4.0	1.0	1.600	6.15 ± 0.40
	5.0	1.0	1.600	8.25 ± 0.40
DMSO	100	1.8	1.301	0.117 ± 0.010
	200	1.8	1.301	0.250 ± 0.020
	300	1.8	1.301	0.333 ± 0.020
	400	1.8	1.301	0.48 ± 0.03
	500	1.8	1.301	0.64 ± 0.05

TABLE VI. Reactions Between $Pt(H_2O)_4^{2+}$ and DMSO. The hydrogen ion concentration was 1.00 M and the wavelength 230 nm or 255 nm.

10^3 C_{DMSO}/M	10^3 C_{Pt}/M	10^5 k_{exp}/s^{-1}
0.60	6.06	0.055 ± 0.001
0.40	4.04	0.035 ± 0.002
0.20	2.02	0.0179 ± 0.0008
50	1.65	0.333 ± 0.013
100	1.65	0.714 ± 0.010
200	1.65	1.55 ± 0.02
350	1.65	2.73 ± 0.03
500	1.65	3.81 ± 0.05
500	0.83	3.90 ± 0.05

(*cf.* Ref. 13) at 230 nm and the concentration of $PtDMSO(H_2O)_3^{2+}$ at the moment of mixing was obtained from the transmittance change for reaction (12). The change of $PtDMSO(H_2O)_3^{2+}$ concentration with time gave the rate constants in Table VI.

Results

Figure 1 shows the observed rate constants *vs.* the concentration of excess entering ligand for the six substrate complexes used. The rate constants obtained from the slopes are given in Table VII. For $PtCl_4^{2-}$ and *trans*-$PtCl_2(H_2O)_2$, chloride is substituted by the entering ligand Y. In the latter case this is due to the large *trans*-effect of chloride compared to water. The other four reactions are anation reactions, in which a water *trans* to chloride is substituted by Y.

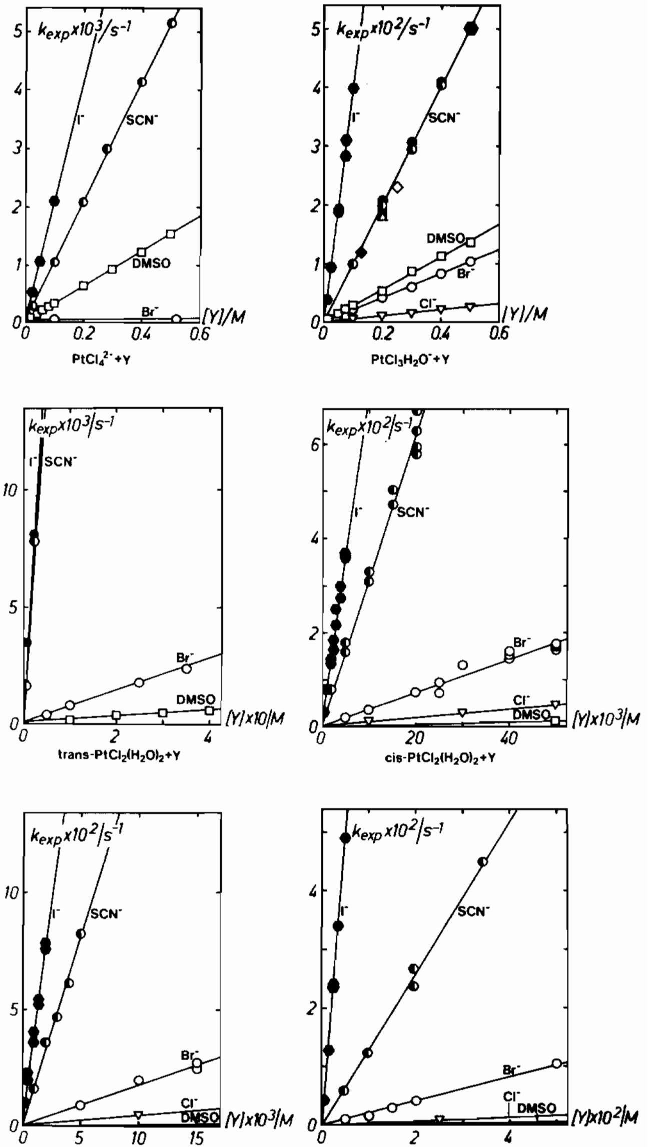
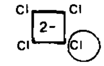
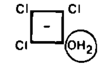
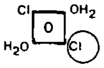
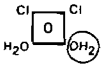
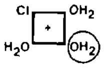
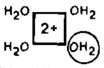


Figure 1. Observed rate constants for reactions (6) to (11), *vs.* concentration of entering ligands, Y. The different symbols for Y = SCN^- refer to different pH.

Figures 2 and 3 show the experiments with $PtCl_4^{2-}$ and *trans*-$PtCl_2(H_2O)_2$ for moderately large concentrations of entering ligand. For the reactions of $PtCl_4^{2-}$ with bromide and thiocyanate and for all the *trans*-$PtCl_2(H_2O)_2$ reactions, the rate constants are

TABLE VII. Rate Constants at 25.0 °C for 1.00 *M* Perchlorate Medium. ○ denotes the leaving ligand.

Reaction No.	Substrate complex \ Entering ligand	$k/s^{-1}M^{-1}$					$k/(nQ^q)/s^{-1}M^{-1}$				
		Cl^-	Br^-	DMSO	SCN^-	I^-	Cl^-	Br^-	DMSO	SCN^-	I^-
(6)		-	$(4.8±0.6)×10^{-5}$	$(3.2±0.2)×10^{-3}$	$(1.00±0.06)×10^{-2}$	$(1.96±0.16)×10^{-2}$	-	$3.0×10^{-4}$	$9.0×10^{-5}$	$6.3×10^{-2}$	0.12
(7)		$(5.2±0.2)×10^{-3}$	$(2.07±0.11)×10^{-2}$	$(2.79±0.10)×10^{-2}$	0.10±0.01	0.38±0.02	$2.6×10^{-2}$	0.10	$9.3×10^{-3}$	0.5	1.9
(8)		-	$(6.7±0.2)×10^{-3}$	$(1.42±0.15)×10^{-3}$	0.30±0.02	0.31±0.03	-	$3.4×10^{-3}$	$7.0×10^{-4}$	0.15	0.16
(9)		$(8.3±0.3)×10^{-2}$	0.35±0.05	$(2.53±0.15)×10^{-2}$	3.15±0.20	7.3±0.5	$4.2×10^{-2}$	0.18	$1.3×10^{-2}$	1.6	3.7
(10)		$0.46±0.03^{a}$	1.7±0.2	$(1.2±0.1)×10^{-2}$	16.0±0.9	39±2	$9.2×10^{-2}$	0.34	$3.6×10^{-2}$	3.2	7.8
(11)		$(2.66±0.04)×10^{-2\,a}$	$0.211±0.003^{a}$	$(8.4±0.5)×10^{-5}$	$1.33±0.02^{a}$	$9.4±0.2^{a}$	$2.7×10^{-4}$	$2.1×10^{-3}$	$1.9×10^{-4}$	$1.3×10^{-2}$	$9.4×10^{-2}$

[a] Values from Ref. 6.

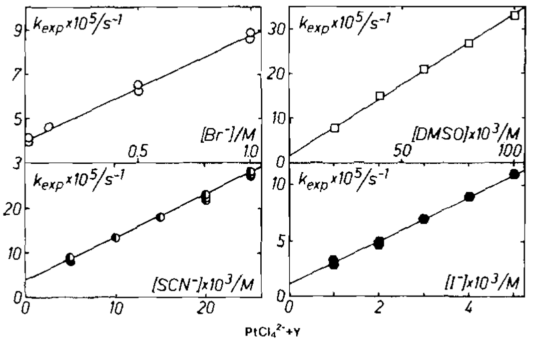


Figure 2. Observed rate constants for reaction (6) for moderately large concentrations of entering ligand. The intercepts correspond to acid hydrolysis rate constants, *cf.* eqns. (5), (13) and (14).

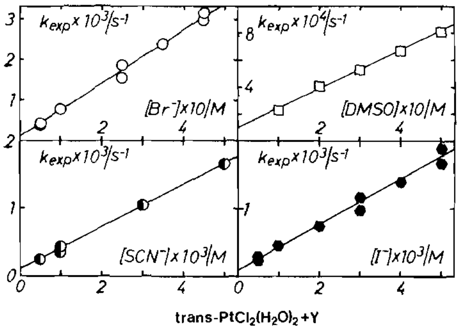


Figure 3. Observed rate constants for reaction (8) for moderately large concentrations of entering ligand. The intercepts give the acid hydrolysis rate constant for *trans*-$PtCl_2(H_2O)_2$.

described by eqn. (5). The intercepts for the $PtCl_4^{2-}$ reactions are (4.0 ± 0.2) × 10^{-5} s^{-1} (Br^-) and (3.8 ± 0.6) × 10^{-5} s^{-1} (SCN^-) which can be identified with the previously determined acid hydrolysis rate constant for $PtCl_4^{2-}$ (3.7 ± 0.2) × 10^{-5} s^{-1} [4]. For the reactions of $PtCl_4^{2-}$ with iodine and DMSO, the observed rate constant is described by eqn. (4) with $X = Cl^-$ and $Y = I^-$ or DMSO. The solutions in Table I have been prepared so that $[Cl^-]/[DMSO] = 10$ for $[DMSO] \leqslant 100$ m*M* and $[Cl^-]/[I^-] = 200$ for $[I^-] \leqslant 5$ m*M*. If we introduce the rate constants k_{-1} and k_3 defined by (3) from Table VII into (4) we arrive at

$$k_{exp} = k_1/2.86 + k_2[DMSO]\,;\qquad [DMSO] \leqslant 100\ mM \tag{13}$$

$$k_{exp} = k_1/3.74 + k_2[I^-]\,;\ [I^-] \leqslant 5\ mM \tag{14}$$

for the experiments with DMSO and iodide, respectively. The intercepts of the two plots in Figure 2 give $k_1/2.86$ = (1.4 ± 0.3) × 10^{-5} s^{-1} (DMSO) and $k_1/3.74$ = (1.09 ± 0.2) × 10^{-5} s^{-1} (I^-), or k_1 = (4.0 ± 0.8) × 10^{-5} s^{-1} (DMSO) and k_1 = (4.1 ± 0.7) × 10^{-5} s^{-1} (I^-), which are again in good agreement with the acid hydrolysis rate constant for $PtCl_4^{2-}$.

Similarly, the *trans*-$PtCl_2(H_2O)_2$ reactions shown in Figure 3 give the intercepts (1.1 ± 0.4) × 10^{-4} s^{-1} (Br^-), (1.0 ± 0.4) × 10^{-4} s^{-1} (I^-), (1.1 ± 0.4) × 10^{-4} s^{-1} (SCN^-), and (1.0 ± 0.3) × 10^{-4} s^{-1} (DMSO) which agree with the previously determined acid hydrolysis rate constant (1.0 ± 0.3) × 10^{-4} s^{-1} for *trans*-$PtCl_2(H_2O)_2$ [6].

The experiments shown in Figure 4 gave the rate constant for reaction (11) as (8.9 ± 0.3) × 10^{-5} M^{-1} s^{-1} for excess platinum and (7.8 ± 0.2) × 10^{-5} M^{-1} s^{-1} for excess DMSO.

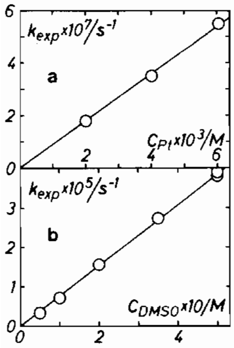


Figure 4. Observed rate constants for reaction (11) *vs.* concentration of excess reactant.

Discussion

The Solvent Path

A comparison of the rate constants for reactions (6) and (7) in Table VII shows that $PtCl_3H_2O^-$ is sufficiently reactive in all cases studied (by a factor 9 to 500) to be an intermediate in the k_1-path of reaction (6) according to model (3). Similarly, a comparison of the rate constants for reactions (8) and (10) shows that $PtCl(H_2O)_3^+$ reacts 9 to 250 times faster with Y than *trans*-$PtCl_2(H_2O)_2$. Moreover, the agreement between the k_1-constants obtained from the intercepts of the plots in Figures 2 and 3 and the separately determined acid hydrolysis rate constants for $PtCl_4^{2-}$ and *trans*-$PtCl_2(H_2O)_2$ supports the interpretation of the k_1-path as due to an associative reaction between the solvent and the complex. The necessary conditions for model (3) are thus fulfilled in both cases.

The rate constants for Y = SCN^- in Table VII indicate clearly that there is nothing "anomalous" with thiocyanate as entering ligand, which has been suggested by Mureinik [5]. Thiocyanate reacts ten times faster with $PtCl_3H_2O^-$ than with $PtCl_4^{2-}$ (and 130 times faster with $Pt(H_2O)_4^{2+}$). The half-life for the $PtCl_3H_2O^-$–thiocyanate reaction is only about 7 s for 0.1 *M* thiocyanate, so the reason for the reported non-reactivity of thiocyanate is probably that equilibrium was already established at the start of the observations in Ref. 5 and/or that the concentrations of complex were too small to give a measurable change of absorbance at the wavelength used.

Cattalini and coworkers [14] have previously reported rate constants for the reaction between $PtCl_4^{2-}$ and Y = Br^-, I^- and SCN^-, which disagree by factors between 3 and 40 with our present results in Table VII. The discrepancy is largest in the case of bromide, since the reaction model used in Ref. 14 with only two rate-determining steps for the overall reaction $PtCl_4^{2-} \rightarrow PtBr_4^{2-}$ is not valid for that system (*cf.* Ref. 15), because the difference in *trans*-effect between chloride and bromide is not sufficiently large. Mureinik [5] reports 1.4 × 10^{-2} M^{-1} s^{-1} for the $PtCl_4^{2-}$–thiocyanate reaction and Kukushkin and Kirillov [11] 2.8 × 10^{-3} M^{-1} s^{-1} for the $PtCl_4^{2-}$–DMSO reaction which agree with our results in Table VII.

Reactivity Correlations

A comparison of the rate constants in Table VII for reaction (9) gives as a first approximation the entering ligand order (15)

$$\begin{array}{l} DMSO < Cl^- < Br^- < SCN^- < I^- \\ 0.3 \quad : 1 \quad : 4 \quad : 40 \quad : 100 \end{array} \qquad (15)$$

for water as leaving ligand and for a neutral substrate complex, where the effect of the charge of the entering ligand is small. A comparison of the rate constants for reactions (8) and (9), where also ionic charge effects are negligible, shows that the ratio between Cl^- and H_2O as leaving ligands depends on the nature of the entering ligand. The ratio Cl^-/H_2O is 0.017 for Y = Br^-, 0.06 for Y = DMSO, 0.1 for Y = SCN^-, and 0.05 for Y = I^-.

We have previously [13, 15, 16] described rate constants for anation reactions by an equation of the type

$$k/n = \kappa \times T \times C_1 \times C_2 \times Q^q \qquad (16)$$

The constant κ is a characteristic for the entering ligand, the leaving ligand, and the central metal ion. The charge factor Q is approximately 5 for chloride and bromide as entering ligands [13, 15, 16]. It is possible by use of the entering ligand order (15) and the relative leaving ligand effect Cl^-/H_2O for the different entering ligands Y to calculate charge factors Q for I^-, SCN^- and DMSO as entering ligands.

For example, the rate constants for reaction (6) for Y = Br^- and DMSO can be described by eqns. (17)

$$4.8 \times 10^{-5}/4 = 4 \times 0.017 \times 5^{-2} \times const.; (Br^-) \qquad (17)$$
$$3.2 \times 10^{-3}/4 = 0.3 \times 0.06 \times Q_{DMSO}^{-2} \times const.; \quad (DMSO)$$

which give Q_{DMSO} = 0.32. Similar calculations using the rate constants for reactions (6), (7), (10) and (11) give Q = 5 ± 1 for I^- and SCN^- as entering ligands in agreement with previous results [6]. For DMSO, a mean value of Q = 0.35 ± 0.1 is obtained, which is reasonable, since DMSO is a polar molecule with a small positive charge at the sulfur atom [17]. The rate constants can now be adjusted for the influence of statistical factors and ionic charge. Table VII contains these values of $k/(nQ^q)$.

Comparison of $k/(nQ^q)$ for reactions (6) and (8), (7) and (10), and (7) and (9) shows that the relative *cis*-effect Cl^-/H_2O is 0.5 ± 0.2, independent of the entering ligand Y. The value agrees with previous findings [13, 15, 16]. Similarly, the relative *trans*-effect Cl^-/H_2O can be calculated from reactions (7) and (11), (9) and (11) and (10) and (11). If a correction for the differences in *cis*-effect is applied, the following values for the relative *trans*-effect Cl^-/H_2O are obtained for different entering ligands Y:

$$\begin{array}{ccccccccc} Cl^- & > & Br^- & \approx & SCN^- & > & I^- & > & DMSO \\ 350 & : & 200 & : & 200 & : & 80 & : & 50 \end{array} \qquad (18)$$

Comparison of $k/(nQ^q)$ for reactions (6) and (7), (8) and (10), (8) and (9), (7) and (8), and (6) and (10) corrected for the *cis*-effects shows that water is a more efficient leaving ligand than chloride, but the relative efficacy H_2O/Cl^- changes with the nature of the entering ligand Y in the following manner:

$$\begin{array}{ccccccc} Br^- & > & DMSO & > & I^- & > & SCN^- \\ \sim 200 & : & \sim 75 & : & \sim 30 & : & \sim 15 \end{array} \qquad (19)$$

Thus, both the relative *trans*-effect Cl^-/H_2O and the relative efficacy of H_2O and Cl^- as leaving ligands depend on the nature of the entering ligand Y, whereas the relative *cis*-effect Cl^-/H_2O is independent of Y. This is consistent with an associative mechanism *via* a trigonal-bipyramidal intermediate, where the *trans*-ligand, the leaving ligand and the entering ligand interact in the trigonal plane around the platinum atom, whereas the *cis*-ligands are at the apices of the bipyramid.

Finally, a comparison of $k/(nQ^q)$ for the other reactions in Table VII show that the entering ligand order (15) is approximately valid for all these reactions*. It is worth noting that DMSO is a poor entering ligand in spite of its relatively large *trans*-effect (2×10^6 relative to water [13].).

From the entering ligand order (15) it is reasonable to expect a rate constant for the $PtCl_4^{2-}$–chloride reaction of about 1×10^{-5} s^{-1} M^{-1}. Such a slow rate for the direct exchange of chloride ligands in $PtCl_4^{2-}$ is compatible with isotopic exchange experiments [10] which indicate a reaction mainly *via* aquation to $PtCl_3H_2O^-$.

Acknowledgements

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*$k/(nQ^q)$ for reactions (6) and (8) must first be adjusted for the difference between Cl^- and H_2O as leaving ligands.